

Comparison of Carbon XANES Spectra from an Iron Sulfide from Comet Wild 2 with an Iron Sulfide Interplanetary Dust Particle. S. Wirick¹, G. J. Flynn², L. P. Keller³, S. A. Sandford⁴, M. E. Zolensky³, K. Nakamura Messenger³, C. Jacobsen¹, ¹Dept. of Physics and Astronomy, SUNY StonyBrook, NY 11794, USA, (swirick@bnl.gov), ²Depart. of Physics, SUNY Plattsburgh, NY 12901 USA, ³NASA Johnson Space Center, Houston, TX, 77058, USA, ⁴NASA AMES Research Center, Moffett Field, CA 94035

Introduction: Among one of the first particles removed from the aerogel collector from the Stardust sample return mission was an $\sim 5 \mu\text{m}$ sized iron sulfide. The majority of the spectra from 5 different sections of this particle suggests the presence of aliphatic compounds. Due to the heat of capture in the aerogel we initially assumed these aliphatic compounds were not cometary but after comparing these results to a heated iron sulfide interplanetary dust particle (IDP) we believe our initial interpretation of these spectra was not correct.

It has been suggested that ice coating on iron sulfides leads to aqueous alteration in IDP clusters which can then lead to the formation of complex organic compounds from unprocessed organics in the IDPs similar to unprocessed organics found in comets [1]. Iron sulfides have been demonstrated to not only transform halogenated aliphatic hydrocarbons but also enhance the bonding of rubber to steel [2,3]. Bromfield and Coville (1997) demonstrated using X-ray photoelectron spectroscopy that “the surface enhancement of segregated sulfur to the surface of sulfided precipitated iron catalysts facilitates the formation of a low-dimensional structure of extraordinary properties” [4]. It may be that the iron sulfide acts in some way to protect aliphatic compounds from alteration due to heat.

Samples: Five ultramicrotomed sulfur embedded sections from particle C2044,0,36,1 from Comet Wild 2 were analyzed. This particle was located in track 36. L2009 is a cluster IDP from cluster 10 collected in the Earth’s atmosphere at a height of ~ 20 km. One ultramicrotomed sulfur embedded section of the iron sulfide from L2009 cluster 10 was analyzed.

Result: The iron sulfide from this IDP cluster was $\sim 3 \times 5 \mu\text{m}$ in size. Besides sulfur and iron; nickel, silicon, magnesium, calcium, aluminum, chromium, and phosphorus were found in the cluster. This iron sulfide was analyzed using both transmission electron microscopy (TEM) with electron diffraction; and scanning transmission x-ray microscopy (STXM) with carbon x-ray absorption near edge structure (XANES) spectroscopy. The TEM results showed a complete rim of magnetite surrounding the iron sulfide core suggesting significant heating upon atmospheric entry. Typically, IDPs showing full-developed magnetite rims also exhibit Zn-loss [5] which occurs above ~ 1100 degrees C in pulse heating of primitive

meteorites [6]. The STXM carbon map (fig. 1a) shows that much of the carbon associated with this particle was pushed off of the particle during microtoming. This is an effect we have observed in other IDP sections. The carbon XANES spectrum from this area suggests a carbon species similar to an amorphous carbon compound with a carbonyl bond to it, (fig.2); an oxygenated amorphous carbon. A C=O bond typically absorbs in the 288-289 eV range. Amorphous carbon has a very broad peak around 285 eV suggesting multiple absorption peaks due to amorphous carbon’s different bonding configurations of sp² C atoms and the tendency of these bonds to gather into pi bond clusters of different bonding configurations [7].

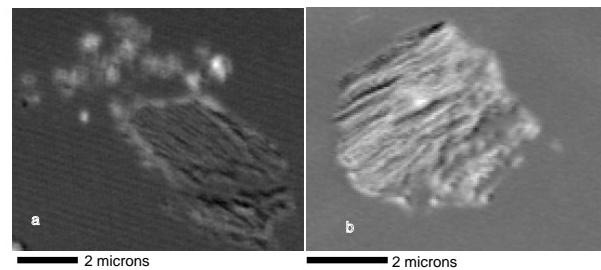


Figure 1. Carbon map of L2009 (a) and Comet Wild 2 particle C2044,0,36,1 (b).

Comet Wild 2 ‘s iron sulfide’s carbon map shows more carbon associated with this sulfide than carbon with the IDP iron sulfide. Only one of the 5 sections has carbon XANES spectra similar to the carbon XANES spectra of L2009 shown in Figure 1 where the carbon species is amorphous with a carbonyl attached (fig.2).

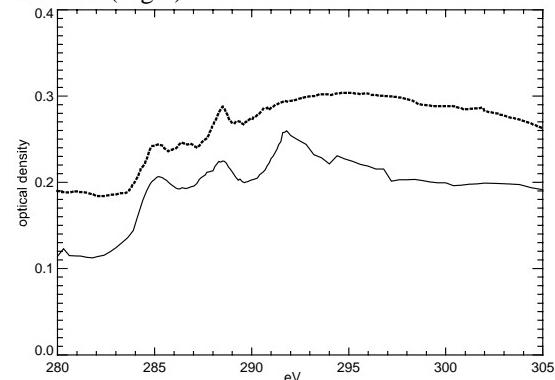
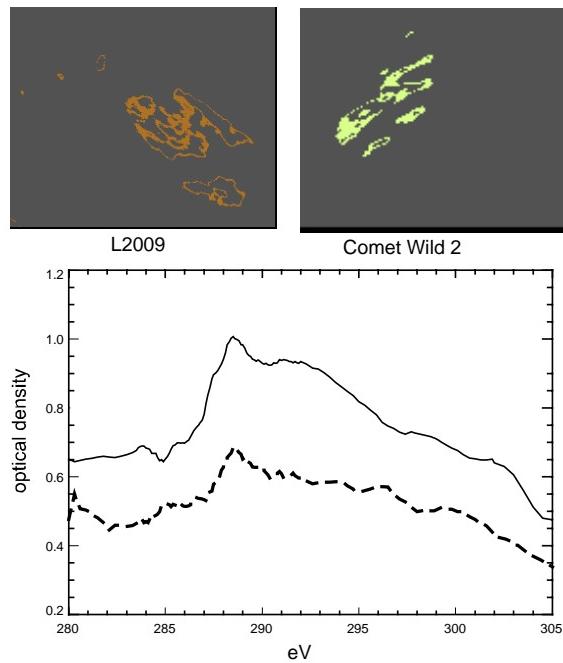


Figure 2. Carbon XANES spectra from iron sulfide in Comet Wild 2 (solid black) and the iron sulfide from IDP L2009 cluster 10.

Figure 3 has cluster analysis images of the iron sulfides from both L2009 and Comet Wild 2 and the spectra from these cluster images. Using STXM, one can collect a series of images of the same area at different energies, the energy spacing in small increments, usually 0.1 eV. From this STACK of images one can apply different mathematical techniques to analyze this data set. Cluster analysis uses a learning vector quantization algorithm with either a Euclidian or angle distant measure on a noise filtered and orthogonalized reduced STACK data set. From this, one obtains a grouping of the data of similar spectral signatures [8].



Fig

ure 3. Cluster grouping of L2009 (top left) with spectrum from this grouping (dotted) and Cluster grouping of Comet Wild 2 and the spectrum from this grouping (solid).

The cluster spectra and images in Figure 3 show the aliphatic compound is associated with the interior of the iron sulfides.

Discussion: The amorphous material found associated with the iron sulfide from Comet Wild 2 was located in both the interior and around the edge of the iron sulfide. This amorphous material was found in only one of the five sections. The aliphatic material was also found in both the interior and on the edge of this iron sulfide. In the case of the iron sulfide from L2009, nearly all of the amorphous material was pushed off of the particle during micromilling suggesting that most of the amorphous carbon was associated with the exterior of the particle and the aliphatic matter with the interior of the particle.

Melted aerogel has been identified in Comet Wild 2 samples (H. Leroux, personnel communication). We know silica aerogel melts at ~1700 ° C [9]. The presence of melted aerogel suggests that at least some of Comet Wild 2's particles must have reached temperatures close to 1700° C. We see both amorphous and aliphatic material associated with the iron sulfide from Comet Wild 2 so there must be some reaction between the iron sulfide with some of the carbonaceous material that inhibits the carbon from forming amorphous or graphitic carbon. We also know that IDP L2009 was severely heated and yet associated with this iron sulfide is an aliphatic material. There is some absorption in the 284-285 eV region of the spectra from Comet Wild 2, this is not a pure aliphatic compound but the absorption in the 287-289 eV region suggests a hydrogenated carbon bond and/or C-O, C=O, COOH. Kerogen heated to 300 ° C with small, <1μm sized clay particles resulted in amorphous carbon plus an aliphatic carbon on the surface of the clay (T. Schaefer, personnel communication).

Conclusions: The carbon XANES spectrum of an aliphatic compound found associated with the interior of an iron sulfide from Comet Wild 2 is similar to carbon XANES spectra from the interior of an IDP iron sulfide. The similarity between this organic matter in the interior of the iron sulfides from Comet Wild 2 and an IDP suggests both contain extraterrestrial organics that may have formed by similar processes, and there is a mechanism where by iron sulfides protect aliphatic matter from becoming amorphous upon heating.

Acknowledgements: This work was supported by Stardust Discovery Data Analysis Program grants NNX07AM856 and NNX07AM78G and NASA Exobiology Program grant NNX07AJ08G. The measurements were performed at the NSLS using the X1A STXM which was upgraded using funds from a SRLIDAP grant NAG512884. The NSLS is supported by the Dept. of Energy.

References: [1]Rietmeijer, F. J. M., (2005), *Advan. Space Res.*,36, 201-208, [2]Butler, E. C.& Hayes, K. F., (2000), *Environ. Sci. Tech.*, 34, 422-429, [3] Delattre, J. L., et al (2006), *Applied Surface Sci.*, 252, 3912-3919, [4] Bromfield, T. C. & Coville, N. J., (1997), *Applied Surface Sci.*, 19, 19-24, [5] Flynn, G. J. et al (1993), *LPSCXXIV*, pt.1:A-F, 497-498 [6] Greshake, (1998), *Meteorites*, 33, 267-290 , [7] Theye, M.L.& Paret, V., (2002), *Carbon* 40, 1153-1166, [8] Lerotic, M. et al, (2005), *J. El. Spec. & Relat. Phen.*, 147, 1137-1143, [9] Zolensky, M.E., et al (2006), *Science*, 314, 1735